## **Description for general public**

CO<sub>2</sub>, an abundant and cheap source of carbon and oxygen, is a key player in the synthesis of various chemicals. This makes its transformation a research hotspot in energy, environmental chemistry, and materials. Electrochemical CO<sub>2</sub> reduction, a cost-effective and environmentally friendly method, can convert CO<sub>2</sub> into chemicals of industrial importance and fuels. The research in this direction is primarily motivated by the search for renewable energy and the need for carbon neutrality. In recent years, we have witnessed significant progress in understanding how different parameters influence the selectivity and efficiency of this process. However, many aspects of the CO<sub>2</sub> reduction mechanism remain to be discovered. CO, considered one of the most cost-effective and valuable products, can be easily separated from the aqueous electrolytes. It can be used as a feedstock to produce many high-value fuels and chemicals. On the other hand, it is toxic, and products like methanol, ethylene, ethanol, or formate would be even more useful. Usually, a mixture of products is obtained, and hydrogen evolution occurs as a competing reaction.

Both experimental and theoretical studies are actively exploring the mechanisms of these processes and proposing optimal catalysts. Gold and platinum electrodes, and more recently, nanomaterials such as nanoparticles and nanoclusters, have proven to be highly efficient catalysts for CO<sub>2</sub> reduction to CO. In the case of gold clusters and nanoparticles, which are the focus of this project, the findings are often conflicting, particularly regarding the overpotential of reduction, mechanistic aspects, efficiency, and the presence of other products besides CO. Researchers have primarily concentrated on the catalytic metal of the electrode, the structure of catalyst nanoparticles, their sizes, shapes, and the ligands protecting the metallic cores. So far, no emphasis has been placed on the role of the architecture of the catalytic layer, including the arrangement of the catalyst particles, the distances between these particles, or the hydrophobicity of the immediate surroundings of the active sites. In our opinion, these aspects require more thorough research, as they affect not only the effectiveness of the CO<sub>2</sub> reduction process but also the type of products obtained. Typical methods used to deposit nanoparticles as catalysts on conductive substrates: evaporation of drops with nanoparticles, spin coating or chemical vapor deposition, do not enable control of the organization of nanoparticles on the electrode or the creation of larger surfaces with an ordered structure of the catalytic layer. These shortcomings of generally used nanoparticle deposition methods inspired us to investigate the impact of the two-dimensional organization of gold nanocluster layers on carbon electrodes on the efficiency of CO production and the possibility of the reduction process occurring to form other products.

## In this project, we aim to answer the following question: What are the factors connected with the architecture of the catalytic film of nanoparticles on the electrode that determine the efficiency of $CO_2$ reduction and control a particular product formation?

We have the right tool for this research. We will achieve control of the architecture of the ultrathin catalytic layer by applying the Langmuir-Blodgett-Schaefer technique for its construction. The technique was originally developed to form single- or multi-component monolayers of amphiphilic molecules at the water-air interface and transfer them to a solid substrate under the control of a given surface pressure. In our approach, the methodology will be used to construct ultrathin layers of gold nanoclusters or mixed layers with copper clusters for catalytic CO<sub>2</sub> reduction. By regulating the surface transfer pressure of the layer and the composition of the layer, we will be able to systematically change the structure of the catalytic film and assess its impact on the course of CO<sub>2</sub> reduction and the products formed. Our previous research on gold nanoparticles and preliminary CO<sub>2</sub> reduction studies confirmed the suitability of the Langmuir-Schaefer technique for producing monolayers of gold nanoclusters and creating durable layers with a given packing on the surface of carbon electrodes. We will examine intermediate and final products using electrochemical methods, surface analysis techniques and commonly used gas and liquid analysis methods. The information obtained as a result of the project will serve as guidelines for the construction of cathodes for practical applications of the CO<sub>2</sub> reduction process.